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Supporting Information

Light-Induced Charged and Trap States in Colloidal Nanocrystals Detected by Variable Pulse Rate Photoluminescence Spectroscopy

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Photoluminescence average lifetime

We define the photoluminescence average lifetime, τ , in the time interval $[0, \infty]$ as:

$$\tau = \int_0^{\infty} \frac{PL(t')}{PL(0)} dt' \quad (1)$$

The suitability of this definition and its consistency with the general definition of average surviving time of an excitation are evident in the case of single-exciton emission. In this

circumstance, the normalized photoluminescence at time t , $PL(t)/PL(0)=n(t)/n(0)$, provides the probability that the emitting excitations survive for times $t' \geq t$ following the pulsed excitation at $t=0$. In other words, $PL(t)/PL(0)$ (proportional to the instantaneous population) represents the cumulative distribution function for the emitting species and is thus related to the probability density function $p(t)$ *via* the general equation:

$$\frac{PL(t)}{PL(0)} = \int_t^{\infty} p(t') dt' \quad (2)$$

In the present specific case, $p(t)dt=-dn/n(0)$ denotes the probability that an exciton decays in the time window $t, t+dt$. It is easy to show with some algebra that the common definition of the average surviving time of the emitting excitations, τ_{ex} , coincides with the photoluminescence average lifetime defined through equation 1, *i.e.*:

$$\tau_{ex} = \int_0^{\infty} p(t') t' dt' = \int_0^{\infty} \frac{PL(t')}{PL(0)} dt' = \tau \quad (3)$$

If the emitting excitation decays exponentially with a characteristic time T , the average lifetime $\tau = \tau_{ex} = T$.

Traps and charges in photoluminescence.

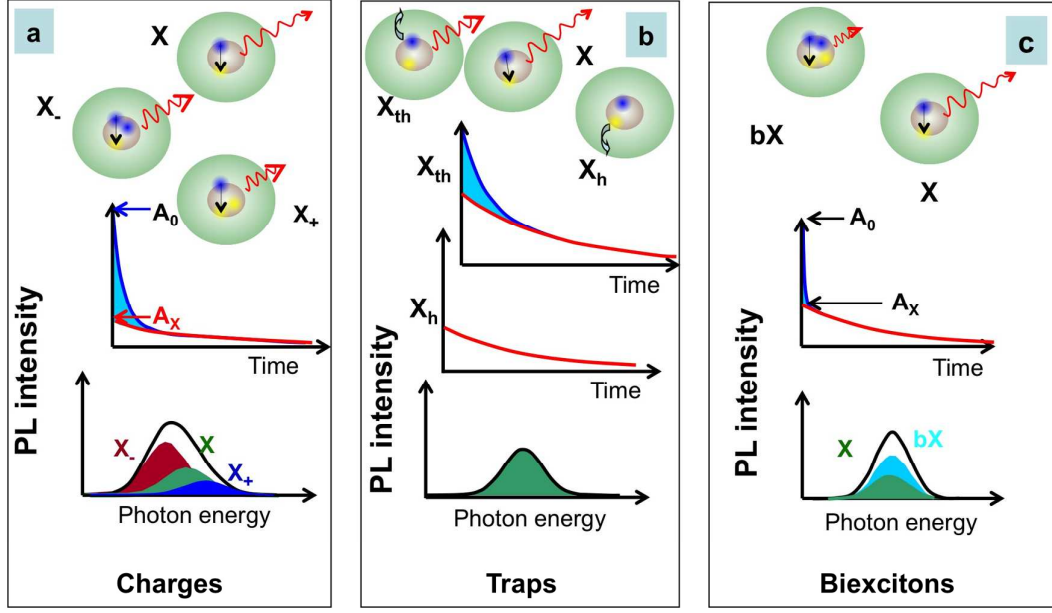


Figure S1. Expected effects of charged states and traps on photoluminescence time traces, as explained in the main text. a) Charged excitons, *i.e.* trions, cause an enhancement of the initial amplitude of the signal A_0 because of their shorter radiative time with respect to excitons; they are also subject to Auger recombination, leaving only the longer-living exciton component after decaying; the emission spectrum of charged and neutral excitons can be distinguished because of the energy shift induced by the exciton-charge interactions. b) Activation of traps instead causes no enhancement of the initial photoluminescence amplitude A_0 ; thermal traps capture excitons already relaxed to the band edge and therefore shorten the initial photoluminescence decay; hot traps capture the exciton before they relax to the band edge and have the only effect of reducing the overall photoluminescence signal, while they leave the dynamics unaltered; as traps subtract excitons and do not emit light themselves, their presence cannot be inferred from the photoluminescence spectrum. c) Biexcitons provide a larger amplitude A_0 and a fast Auger recombination decay; in our samples, biexcitons have zero binding energy and their optical emission cannot be distinguished in spectrum from the excitonic one.

Single shot measurements

As a reference for variable pulse rate photoluminescence spectroscopy, we devise an experiment for nanocrystals in toluene dispersion where every laser pulse excites a fresh portion of sample. Nanocrystal dispersion is flowed through a quartz cylindrical tube, 1 mm in diameter (d), by means of a peristaltic pump. The resulting flow regime is laminar, with Reynolds number ≈ 200 and mean drift velocity $\langle v \rangle = 130$ mm/s. According to fluid mechanics, the nanocrystal motion in the pipe has the parabolic velocity profile sketched in Fig. S1. The solution in direct contact with the wall is still, while the maximum speed, $2 \langle v \rangle$, is reached at the center of the tube. In this region, resulting fluid displacement between two consecutive laser pulses is four times the laser spot size, $\phi = 130$ μm . We calculate that the regime of single pulse excitation is achieved in most (93 %) of the photoexcited volume. Only 3, 1.5 and 0.08 % of the dots undergo two-, three- and four-pulse excitation, respectively. Attenuation of the photoluminescence emitted from the thin layer close to pipe surfaces is provided by confocal light collection of the streak-camera through optical spatial filtering.

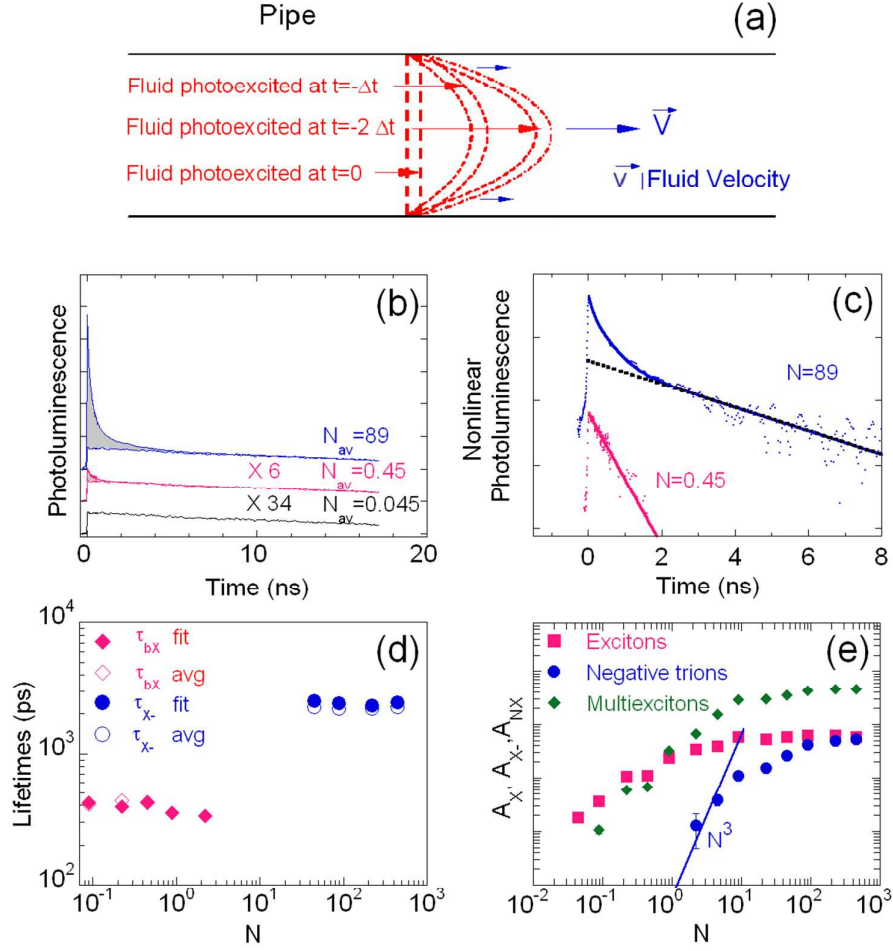


Figure S2. a) A scale cross-section of the cylindrical pipe used to flow the nanocrystal solution. The photoexcited region moves from left to right, ensuring that only a small fraction of nanocrystals, close to the walls of the tube, undergoes multi-pulse excitation; b) Transient photoluminescence signal for three different excitation levels. Gray regions between the photoluminescence curves and the decaying baseline highlight the nonlinear contribution arising from multiexcitons and charge-split states. The baseline is provided by the photoluminescence recorded at $N=0.045$, rescaled to match the long-time signal at the fixed excitation level. Panel c) shows the nonlinear transients (dots), *i.e.*, the difference between the photoluminescence signal at a set N and the baseline, and the corresponding fitting curves (continuous lines). The slowly decaying contribution due to charge-split states is also reported. Panel d) shows the negative trion lifetime, τ_{X-} , estimated through an

exponential fit (full red squares) to the long time signal ($T > 2$ ns) in the high excitation regime ($N > 10$). τ_X is compared with the mean lifetime of the nonlinear signal (empty red squares), evaluated for delay times between 2 and 8 ns. τ_{bX} is biexciton lifetimes, estimated through an exponential fit of the nonlinear photoluminescence in the low and moderate excitation regime (full blue circles). τ_{bX} is compared with the mean lifetime of the nonlinear signal (empty blue circles), ($T < 2$ ns). Panel e) shows the contributions of negative trions and excitons to the nonlinear photoluminescence as a function of the laser fluence. The straight line represents a guide to the eye showing cubic power dependence.

Light emission properties of nanocrystals are investigated as a function of laser fluence. The average number of injected excitons per pulse in each nanocrystals, N , ranges from 0.01 to 500. The transient luminescence signal emitted at the nanocrystal band edge is reported in Fig. S1(a) for three values of laser intensity, corresponding to $N=0.045$, 0.45 and 89, representative of: i) the low excitation regime, achieved for $N \ll 0.1$, with the majority of nanocrystals in the ground state, and only a few excited with a single electron-hole pair; ii) the intermediate excitation regime, with the quantum dots in the ground, exciton or biexciton state, with a negligible probability of finding higher order multiexciton states; iii) the high excitation regime, in which $N \gg 1$ and almost all nanocrystals are multiply excited with average multiplicity N . For $N \ll 0.1$, photoluminescence decays exponentially, with a characteristic time of 21 ns, equal to the exciton lifetime τ_X . In the intermediate excitation regime, a sub-nanosecond decay emerges on top of the long-lived exciton signal. At higher injection levels, the fast transient becomes the dominant contribution. In addition to this component, a further luminescence signal with a nanosecond decay transient appears.

Excitons, biexcitons and multiexcitons, including charged states, can radiatively decay emitting a photon at the optical gap, as a result of the optical transition from the lowest conduction energy level, $1S_e$, to the highest valence level, $1S_h$. Under impulsive excitation, the resulting band edge photoluminescence can be decomposed as the sum of the exciton signal plus the contribution from

all other neutral and charged multiple exciton states. The nonlinear photoluminescence (NLPL) is thus obtained by subtracting the single exciton decay curve, $A_x(t)$, from the overall PL intensity. The transient in the low excitation regime $N=0.045$ is taken as the reference function $A_x(t)$ up to a multiplicative constant, determined by matching the long-time behaviour of $A_x(t)$ and $PL(t)$ for any fixed excitation level. This operation is justified by the fact that the exciton lifetime is at least one order of magnitude longer than the decay time of any other state involved.

The lifetime τ_{NLPL} of the NLPL in the medium excitation regime provides the most reliable estimate of the biexciton lifetime τ_{bX} . NLPL transients are fitted with a single exponential and the resulting values for $N < 4$ are reported in Fig. S1(c). For $N > 0.5$, τ_{NLPL} decreases as the contribution of multiexciton states with shorter Auger lifetimes becomes more important. $\tau_{bX}=0.41 \pm 0.03$ ns is estimated as the average value of τ_{NLPL} for $N_{av} < 0.5$. The same approach is used to establish the lifetime of the long-lived contribution to the NLPL observed in the high excitation regime. The analysis is done for delays longer than 2 ns, when contributions from biexcitons and multiexcitons are negligible. The inset of Fig. S1(d) reports the values of τ_{NLPL} estimated at the highest excitations featuring high signal-to-noise ratio. The long-lived state is assigned to states with reduced Auger recombination rates, negative trions. This attribution is consistent with the fact that the PL emission at these delay times is slightly shifted to the red, as expected for negative trions (see main text). $\tau_{X-}=2.4 \pm 0.1$ ns, about 6 times τ_{bX} , is estimated as the average value of τ_{NLPL} .

In the relaxation-time approximation, band edge photoluminescence following impulsive excitation can be decomposed as the sum, $\sum_i A_i e^{-t/\tau_i}$, of the emitted light intensity from all excited states. Contributions A_i to the PL signal from excitons (A_X) and trions (A_{X-}) are reported in the inset of Fig. S1(d) as a function of the mean number N of excitons injected into nanocrystals. At any laser fluence, A_X is taken equal to the rescaled exciton function $A_x(t=0)=A_0$ shown in Fig. S1(a). A least square fit to the NLPL with the sum of three exponentials measures the relative contributions

of negative trions, biexcitons, and fast-decaying multiexcitons states of order $m > 2$. Representative fit curves are reported in Fig. S1(b). Lifetimes of biexcitons and trions are fixed to the experimental values τ_{bX} and τ_{X-} , independently determined. The free parameters are A_{bX} , A_{mX} (introduced for accounting emission from multiexciton states with $m > 2$) and A_{X-} . A lifetime of 100 ps is used for multiexciton states. Assessments of A_X and $A_{bX} + A_{mX}$ are unaffected by this latter choice. Reliability of fits is checked by analysing the noise pattern. Residuals of all fits to experimental data has a root mean square fluctuations limited by the intrinsic noise of the nonlinear technique, in large part due to the fact that the nonlinear signal is obtained as difference between the overall photoluminescence signal and the excitonic contribution.

According to the discussion reported in the main text concerning the saturation behaviour of the charge population, nanocrystal photoionization is primarily triggered by Auger processes. We use the single-pulse experimental data, in which pulse-to-pulse charge accumulation is precluded, to extract the probability that the Auger nonradiative decay of a multiexciton state leads to the formation of a band-edge trion state. In order to observe photon emission from a trion state in a single-pulse experiment, we should at least consider a tri-exciton state ($m=3$, tX). Auger relaxation of a biexciton state can in fact only lead to a non-radiative charged state with just a single electron (hole) in the nanocrystal core. The probability to excite a tri-exciton state is provided by the Poisson statistics $p(3,N) \sim N^3/6$. tXs mainly relax through Auger processes; if η is the production yield of negative trions per Auger process, the photoluminescence emission intensity A_{X-} reads:

$$A_{X-} = k_{sc} \frac{\tau_{rad,X}}{\tau_{rad,X-}} \frac{N^3}{6} \eta \quad (4)$$

where the scaling factor, k_{sc} , takes into account the exciton radiative decay rate and the detection sensitivity of the experimental set-up and satisfies the relation $A_X = k_{sc}N$; $\tau_{rad,X}/\tau_{rad,X-}$ accounts for the different radiative decay times of excitons and trions. According to the statistical model of non-interacting electrons and holes, $\tau_{rad,X}/\tau_{rad,X-} = 2$.¹ k_{sc} is measured by fitting the low-fluence

photoluminescence intensity *versus* pulse fluence. $\eta=1.4 \times 10^{-3}$ is obtained by fitting the dependence of A_{X-} on N , as reported in Fig.S1(d). At the pulse repetition frequency $\nu=4$ MHz, the population of negative trions is in a quasi-steady state, and well below saturation, n_- reads:

$$n_- \cong p(2, N) \nu \eta \tau_- n_{sat} \cong \frac{N^2}{2} \nu \eta \tau_- n_{sat} = N^2 \nu \alpha \tau_- n_{sat} \quad (5)$$

For the parameter α , defined according to equation 1 reported in the main text, we therefore obtain: $\alpha=\eta/2=7 \times 10^{-4}$.

Thermal effects

In this paragraph it is discussed why thermal effects, *i.e.* warming of the nanocrystals because of laser excitation, are not contributing significantly to the observed charging dynamics of nanocrystals. Nanocrystal warming can be directly detected with our spectroscopy measurements, precisely through spectral broadening and shift of the exciton emission: such manifestations of higher temperature should be present even for long delays after laser pulse excitation and therefore we are able to quantify them by measuring the photoluminescence 10 or more nanoseconds after laser pulse arrival, when all nonlinear effects are over and only single excitons are left with a temperature in equilibrium with the nanocrystal lattice. All our data show instead that the peak wavelength, linewidth and lifetime of the nanocrystal photoluminescence integrated from 20 ns to 50 ns after optical excitation are completely independent of the laser pulse repetition rate and energy. Such behavior rules out significant warming of the samples.

To provide a quantitative bound for thermal effects, we demonstrate now the temperature sensitivity of time-resolved photoluminescence used as a thermometer of the nanocrystal temperature. We prepared nanocrystal toluene dispersion freshly prepared with the same concentration as used in the main measurements reported in the main text. We then measured time-

resolved photoluminescence for 8 KHz and 4 MHz laser repetition rates at the highest available excitation rate, corresponding to an excitation level of N around 0.2. We repeated measurements after warming the solution to a temperature of 70 C in a stabilized hot bath, *i.e.*, 49 K higher than the room temperature. The emission spectrum integrated from 20 ns to 50 ns after optical excitation is clearly different for the two different temperatures; the wavelengths of emission peaks for the two temperatures, obtained with gaussian fits of the emission spectra, are separated by 4.4 nm. Given that warming by 49 K produced a 4.4 nm shift, the temperature dependence of the peak wavelength is 0.09 nm/K. On the other hand, peak wavelengths for the same temperature, but different repetition rates are within 0.35 nm. According to the measured temperature dependence, we can safely state that the highest laser pulse repetition rate and energy that we employed in our experiment does not warm the solution by more than 4 K.

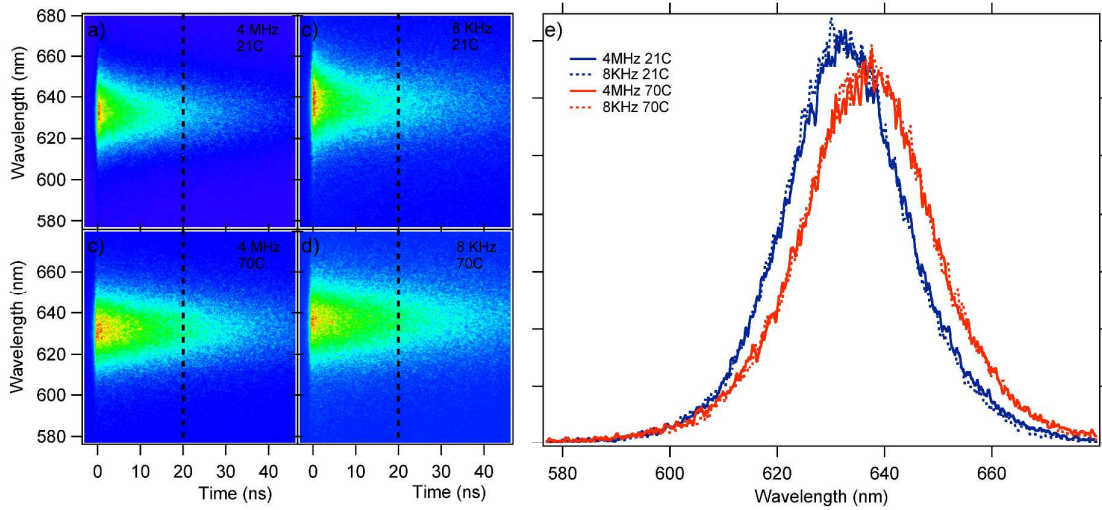


Figure S3. Panels a)-d): spectrograms of the photoluminescence emitted by nanocrystals with repetition rates and temperatures as indicated in the top right corner of each panel. The dashed line indicates the starting time for the integration window (the other integration extreme is not indicated since it coincides with the end of the scan). Panel e): photoluminescence spectra extracted from panels a) to d) by integrating from 20 ns to 50 ns. Spectra were normalized by their area, so that a broadened spectrum will appear lower in peak value.

Model

In the following, we briefly outline the theoretical rate equation model used to quantitatively analyze variable pulse rate photoluminescence data. We assume that each laser pulse excites an ensemble of nanocrystals consisting of: neutral quantum dots in the electronic ground state, negatively or positively charged nanocrystals and nanocrystals with active surface states able to trap hot and thermal photoexcited charges. Populations of these quantum dot states, n_0 , n_- , n_+ , n_h , and n_{th} , respectively, satisfy the conservation rule $n_0 + n_- + n_+ + n_h + n_{th} = 1$. Each n_i depends on the pulse fluence and repetition rate, and slowly varies with time. Absorption of one or more photons from each laser pulse excites a transient population of excitons (n_X), trions (n_{X-} and n_{X+}), neutral and charged multi-excitons. Exciton states of higher multiplicity ($m > 2$) quickly annihilate *via* fast Auger process to form band-edge two-exciton or charged exciton states. The resulting burst of band-edge photoluminescence is characterized by a prompt signal A_0 , which is a linear combination of the populations of the initial nanocrystal states, n_i :

$$A_0 = k_{SC} \left\{ p(1, N) n_0 + p(1, N) n_{th} + \frac{\tau_{rad, X}}{\tau_{rad, X-}} p(1, N) n_- + \frac{\tau_{rad, X}}{\tau_{rad, X+}} p(1, N) n_+ \right. \\ \left. + \sum_{m=2}^{\infty} p(m, N) \left[(n_0 + n_{th}) \frac{\tau_{rad, X}}{\tau_{rad, bX}} + n_- \frac{\tau_{rad, X}}{\tau_{rad, bX-}} + n_+ \frac{\tau_{rad, X}}{\tau_{rad, bX+}} \right] \right\} \quad (6)$$

The first term in equation 4 gives the intensity of the light emitted from neutral, trap-free nanocrystals, which is proportional to the population n_0 and the probability $p(1, N)$ to excite a single exciton, provided by the Poisson distribution $p(m, N)$, where N is the average number of electron-hole pairs excited per quantum dot and m electron-hole pairs are excited in a single nanocrystal. The scaling factor, k_{SC} , takes into account the exciton radiative decay rate and the detection sensitivity of the experimental set-up. Similarly, the second term provides the emission signal from neutral quantum dots with thermal-charge traps. The third and fourth terms concern the

photoluminescence intensity of trion states created in charged nanocrystals. The fifth term describes emission from neutral and charged biexcitons states. The ratios $\tau_{\text{rad},X}/\tau_{\text{rad,bX}}$, $\tau_{\text{rad},X}/\tau_{\text{rad,bX-}}$, $\tau_{\text{rad},X}/\tau_{\text{rad,bX+}}$, $\tau_{\text{rad},X}/\tau_{\text{rad,X-}}$ and $\tau_{\text{rad},X}/\tau_{\text{rad,X+}}$ are set, respectively, to 4, 6, 6, 2 and 2, according to the statistical model of non-interacting electrons and holes, which provides results in good agreement with the available experimental data in CdSe/CdS core/shell nanocrystals.^{s1} Nanocrystals with hot-charge trap states do not contribute to the photoluminescence signal. The amplitude of the long-lived emission is generated in trap-free neutral quantum dots n_0 can be expressed as:

$$A_X = k_{\text{SC}} \left[\sum_{m=1}^{\infty} p(m, N) \right] n_0 = k_{\text{SC}} \left[\sum_{m=1}^{\infty} p(m, N) \right] (1 - n_- - n_+ - n_{th} - n_h) \quad (7)$$

The statistical factor takes into account that electron-hole pair states with $m \geq 2$ nonradiatively relax to the single-exciton state and thus also contribute to the long-decaying signal. At low pulse intensities ($N < 0.03$ excitons per dot), experimental data show that only the long-lived single-exciton emission was detected ($A_0 \cong A_X$) and the photoluminescence signal scales linearly with the injected electron-hole pairs.

Populations n_i are assessed from equations (4) and (5) as follows. Firstly, linear fits to experimental data are performed to assess the scaling factor k_{sc} for each experimental photoluminescence series. For $t > \tau_{\text{bX}} = 0.41$ ns, the photoluminescence signal can be safely ascribed to radiative recombination of neutral and charged excitons alone, as the lifetimes of charged biexcitons as well as neutral and charged multiexcitons are shorter than τ_{bX} . We therefore determine the trion photoluminescence intensity $PL_{X_{-,+}}(t)$ by fitting the photoluminescence spectrum at time $t = 0.6$ ns after laser pulse. The amplitude of trion photoluminescence contribution,

$A_{X_{-,+}}$ is then obtained through the equation: $PL_{X_{-,+}}(t) = A_{X_{-,+}} e^{-\frac{t}{\tau_{X_{-,+}}}}$, with $t = 0.6$ ns.

The steady-state population of the charged nanocrystal state n_- and n_+ are derived from the linear equation:

$$A_{X_{-,+}} = k_{SC} \frac{\tau_X}{\tau_{X_{-,+}}} \left[\sum_{m=2}^{\infty} p(m, N) \right] n_{-,+} \quad (8)$$

This relation results from the fact that negative trions can be created directly or indirectly *via* Auger relaxation of charged multiexciton states ($m \geq 2$).

Once the total population of charged nanocrystals is known, linear equation (7) is used to assess the total population $n_t = n_h + n_{th}$ of trap states. From the knowledge of n_t and the experimental value of the prompt photoluminescence response A_0 , we finally determine n_h and n_{th} by using linear equation (6) and $n_t = n_h + n_{th}$.

Photoluminescence transients vs pulse fluence at $\nu = 4$ MHz

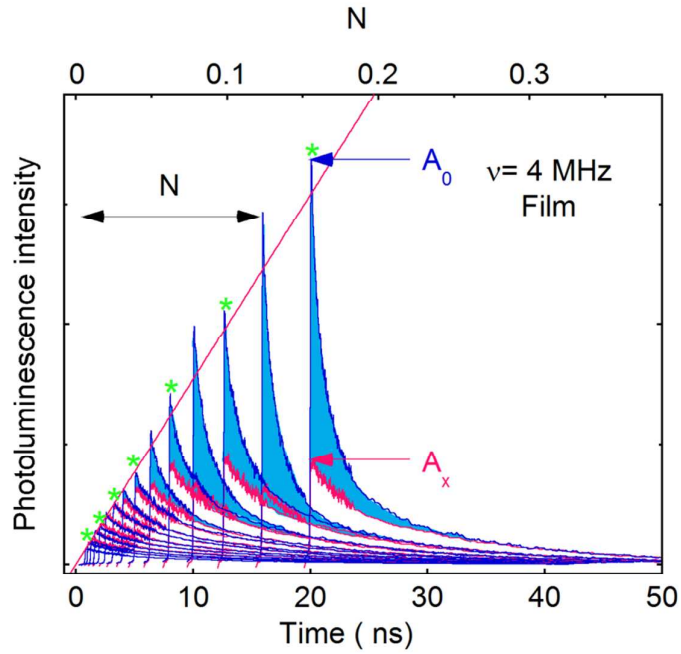


Figure S4. Photoluminescence decays (blue lines) excited at 4 MHz repetition rate are shown for growing pulse fluence. Red lines represent the excitonic contribution to the photoluminescence signal. Transient emission traces are shifted to the right proportionally to the pulse excitation energy. Scans for different intensities are always collected with the same streak camera parameters, notably with the same gain in the microchannel plate; in order to ensure linearity, the only acquisition parameter that is adjusted from one scan to the other is acquisition time. The average number, N , of injected electron-hole pairs per dot corresponding to each PL trace can be read on the upper x axis. The red straight line is a linear fit to the dependence of the prompt photoluminescence intensity on the pulse fluence in the low excitation regime ($N < 0.025$). At higher pulse energies ($N > 0.05$), photoluminescence is strongly quenched. Transient emissions are recorded in two different pulse-energy scans. The second one is acquired two hours later; the corresponding traces are marked by green asterisks. For high pulse fluences, the photoluminescence response observed in the first scan shows a slightly larger enhancement of the prompt response, A_0 , (with respect to a linear dependence on the pulse-energy), but a more efficient quenching of the emission signal at long delays, *i.e.*, lower A_x values.

References for Supplementary Information

(S1) Klimov, V.; McGuire, J.; Schaller, R.; Rupasov, V. Scaling of multiexciton lifetimes in semiconductor nanocrystals. *Physical Review B* **2008**, *77*, 1-12.